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HYDANTOIN OR THIOHYDANTOIN DERIVATIVES AND GERMICIDES FOR  
AGRICULTURAL AND HORTICULTURAL USE  
[Hidan'toin' mataha Chiohidan'toin' no Yudotai oyobi Noen'geiyo  
Sakkin'zai]

Osamu Wakabayashi, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE  
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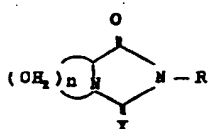
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## 1. Title

Hydantoin or Thiohydantoin Derivatives and Germicides for  
Agricultural and Horticultural Use

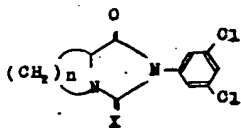
## 2. Claims

(1) 1,5-alkylene-hydantoin or 1,5-alkylene-2-thiohydantoin  
derivatives that are represented by the following general  
formula:



(wherein X is O or S; R is a phenyl group that may be substituted with one or more nitro groups, halogen atoms, lower alkyl groups, lower alkoxy groups, trifluoromethyl groups, or chlorobenzyloxy groups or a naphthyl group; and n is 3 or 4, provided that, when X is S and n is 4, R is not a monochlorophenyl group or a p-tolyl group.)

(2) Germicides for agricultural and horticultural use whose active ingredient is a hydantoin or thiohydantoin derivative that is represented by the following general formula:



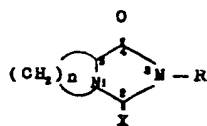
(wherein X is O or S and n is 3 or 4).

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### 3. Detailed Description of the Invention

The present invention pertains to 1,5-alkylene-hydantoin or 1,5-alkylene-2-thiohydantoin derivatives that are represented by the following general formula:



(wherein X is O or S; R is a phenyl group that may be substituted with one or more nitro groups, halogen atoms, lower alkyl groups, lower alkoxy groups, trifluoromethyl groups, or chlorobenzyloxy groups or a naphthyl group; and n is 3 or 4, provided that, when /878 X is S and n is 4, R is not an o-, m-, or p-chlorophenyl group or a p-tolyl group.)

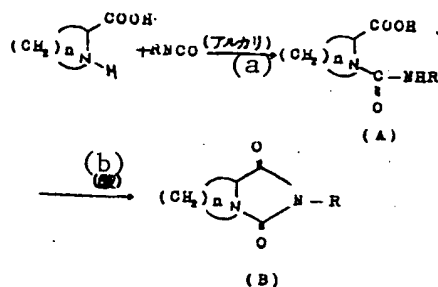
The present inventors had been studying the herbicidal activities of 3-substituted hydantoins and learned that new compounds that have alkylene groups at the 1- and 5-positions of the hydantoin structure, as shown in the above formula, have superior herbicidal and germicidal effects as well as other desirable properties, such as better conformability to plants (in other words, a proper balance between the lipophilic and hydrophylic properties) and an increased tendency of being nonpoisonous after the application.

The major portion of the structure of the aforesaid compounds is proline or pipecolic acid. Proline, especially L-proline, is an essential amino acid for humans and is present throughout the natural world. L-pipecolic acid is also known to

be a lysine metabolite and also known to exist in apples, green beans, and other plants. This suggests that the compounds of the present invention have a high potential for solving environment-related problems. The present invention was achieved based upon this knowledge.

The hydantoin derivatives of the present invention can be obtained, for example, by reacting proline or a pipecolic acid with isocyanate or isothiocyanate according to a conventional method. The following reaction formula represents this reaction.

(i) When  $X = O$ ,

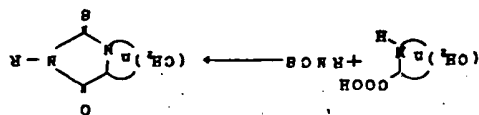


Key: a) alkali; b) acid.

(wherein R has the above-defined meaning.)

A salt of proline or a pipecolic acid that is suspended or dissolved in a water-solvent (such as benzene, chlorobenzene, ether, DMF, etc.) system reacts with isocyanate to yield hydantoic acid (A). This compound (A) is then heated (80 to 150°C) in the presence of acid (such as hydrochloric acid, sulfuric acid, etc.), thus undergoing dehydrative cyclization. The hydantoin thus produced is refined by such a method as recrystallization, chromatography, distillation, etc.

(ii) When  $X = S$ ,



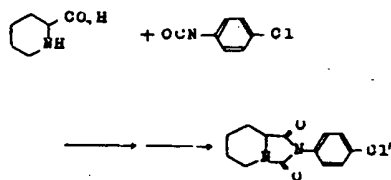
Proline or pipecolic acid and isothiocyanate are heated and refluxed in an appropriate solvent (such as methanol, ethanol, isopropyl ether, THF, DMF, benzene, toluene, etc.), with the addition of acid if needed, thereby obtaining hydantoin derivatives at a high yield. They can be refined in the same manner as in the case of  $X = O$ .

(In the formula, R has the above-defined meaning.)

Various preparation methods have been proposed for proline, and preparation methods by fermentation are also well known. Pipecolic acid can be obtained readily by hydrogenation of picolinic acid.

The following presents some concrete preparation examples of the compounds of the present invention as reference examples.

#### Reference Example 1



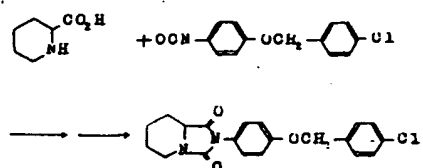
To an aqueous mixture of 1.94 g (0.015 mol) of pipecolic acid, 0.6 g (0.015 mol) of sodium hydroxide, and 25 mL of water was added 2.30 g (0.015 mol) of p-chlorophenyl isocyanate dissolved in 20 mL of chlorobenzene while the mixture was stirred. 879

Four hours later, the reaction solution was extracted twice with 20 mL of ether and acidified by adding concentrated hydrochloric acid to the water phase, thereby depositing a colorless solid. This suspension was heated and refluxed for 1 hour while it was stirred and subsequently cooled to room temperature. After the precipitate was collected by filtration and washed with water, it was recrystallized from isopropanol, thereby obtaining 3.22g of the aforesaid 3-(p-chlorophenyl)-1,5-tetramethylene hydantoin (yield: 81.1 %). Melting point: 157-8° C.

Elemental Analysis Results (of  $C_{13}H_{13}O_2N_2Cl$ )

	C	H	N	Cl
Calculated:	58.98	4.95	10.58	13.40
Found:	59.11	4.96	10.42	13.46

Reference Example 2



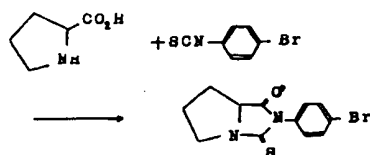
To an aqueous mixture of 1.29 g (0.01 mol) of pipecolic acid, 0.4 g (0.01 mol) of sodium hydroxide, and 20 mL of water was added 2.60 g (0.01 mol) of p-chlorobenzyl isocyanate dissolved in 10 mL of DMF while the mixture was stirred. Four hours later, the reaction solution was acidified by adding concentrated hydrochloric acid to it and subsequently heated and refluxed for 2 hours while it was stirred, and it was then left standing to cool. Thereafter, the precipitate was collected by filtration and washed with water, and it was then recrystallized

from DMF-ethanol, thereby obtaining 2.93 g of the aforesaid 3-[4-(p-chlorobenzoyloxy)phenyl]-1,5-tetramethylene hydantoin (yield: 79.0 %). Melting point: 152-3° C.

Elemental Analysis Results (of  $C_{20}H_{19}O_{[illegible]}N_2Cl$ )

	C	H	N	Cl
Calculated:	64.78	5.17	7.56	9.56
Found:	64.72	5.01	7.43	9.55

Reference Example 3

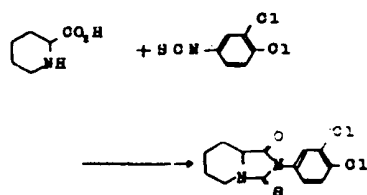


To a mixture of 1.15 g (0.01 mol) of proline and 15 mL of ethanol was added 2.14 g (0.01 mol) of p-bromophenyl isothiocyanate, and the entire mixture was subsequently heated and refluxed for 1 hour over a hot bath. After it was left standing to cool, the precipitated crystal was collected by filtration, and it was recrystallized from ethyl acetate-ethanol to yield 2.60 g of the aforesaid 3-(p-bromophenyl)-1,5-trimethylene-2-thiohydantoin (yield: 83.6 %). Melting point: 159.5-161° C.

Elemental Analysis Results (of  $C_{12}H_{11}ON_2SCl$ )

	C	H	N	S	Cl
Calculated:	46.31	3.56	9.00	10.30	25.68
Found:	46.08	3.29	8.78	10.29	25.59

Reference Example 4





To a mixture of 1.29 g (0.01 mol) of pipecolic acid and 15 mL of ethanol was added 2.04 g (0.01 mol) of 3,4-dichlorophenyl isothiocyanate, and the entire mixture was heated and refluxed for 20 minutes over a hot bath. After it was left standing to cool, the precipitated crystal was collected by filtration, and it was recrystallized from DMF-ethanol to yield 2.78 g of the aforesaid 3-(3,4-dichlorophenyl)-1,5-tetramethylene-2-thiohydantoin (yield: 88.3 %). Melting point: 219-222° C.

Elemental Analysis Results (of  $C_{13}H_{12}ON_2SCl_2$ )

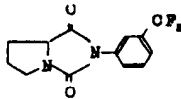
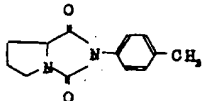
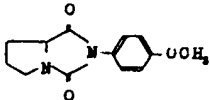
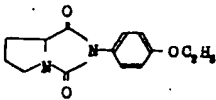
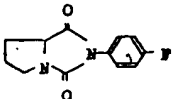
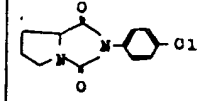
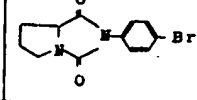
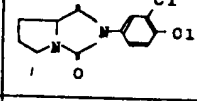
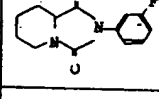
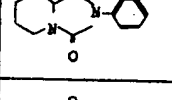
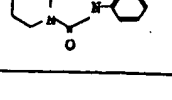
	C	H	N	S	Cl
Calculated:	49.53	3.84	8.89	10.17	22.50
Found:	49.19	3.76	8.78	10.06	22.76

Table 1 in the following shows concrete examples of the hydantoin compounds of the present invention.

In the table under the heading of the elemental analysis, calculated values are presented in the top row, and the found values in the bottom row.

TABLE 1

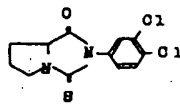
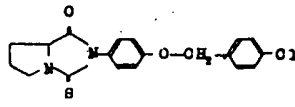
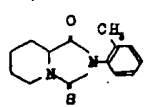
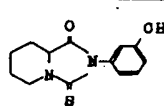
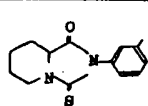
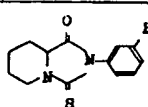
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Compound No.	Structural Formula	Melting Point	Elemental Analysis			
1		133-6	54.93	3.90	9.86	
			55.07	3.88	9.71	
2		158-60	67.81	6.13	12.17	
			67.58	5.96	12.11	
3		124-5	63.40	5.73	11.38	
			63.61	5.77	11.35	
4		121-2	64.60	6.20	10.76	
			64.51	6.18	10.70	
5		142.5-4.5	61.53	4.73	11.96	
			61.61	4.88	11.69	
6		138.5-9.5	57.49	4.42	11.18	X=Cl
			57.41	4.39	11.09	14.14
						14.28
7		174-6	48.83	3.76	9.49	X=Br
			48.61	3.70	9.36	27.08
						27.14
8		142-3	50.55	3.54	9.83	X=Cl
			50.51	3.50	9.60	24.87
						24.61
9		117-8.5	62.89	5.28	11.29	
			62.75	5.26	11.35	
10		132-3	58.98	4.95	10.58	X=Cl
			58.90	4.86	10.32	13.40
						13.51
11		138-9	50.50	4.24	9.06	X=Br
			50.34	4.02	9.13	25.85
						25.79

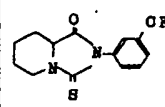
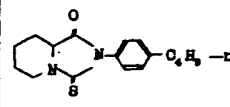
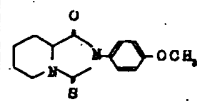
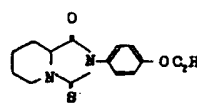
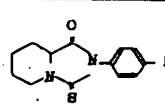
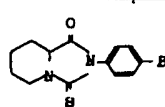


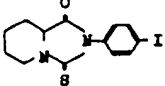
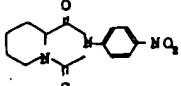
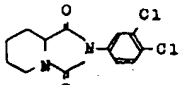
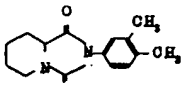
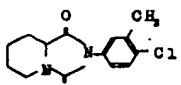
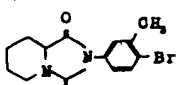
24		155-6	69.74	7.02	10.85	
			69.68	7.11	10.72	
25		172-3	60.32	5.42	10.05	X=Cl
			60.29	5.41	10.01	12.72 12.81
26		186.5-8	52.02	4.68	8.67	X=Br
			51.89	4.68	8.51	24.73 24.91
27		152-3	64.78	5.17	7.56	X=Cl
			64.72	5.01	7.43	9.56 9.55
28		169-71	50.55	3.54	9.83	X=Cl
			50.43	3.47	9.95	24.87 24.78
29		97-9	52.19	4.04	9.37	X=Cl
			52.28	4.19	9.40	23.71 23.88

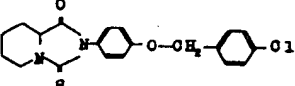
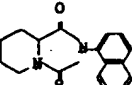
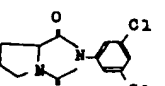
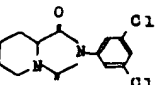
底	構 造 式	(C)	O	H	N	B	X
30		125-7	51.99	3.69	9.33	10.68	
			51.76	3.61	9.25	10.66	
31		213-4.5	63.38	5.73	11.37	13.02	
			63.39	5.71	11.29	13.10	
32		181-3	59.52	5.38	10.68	12.22	
			59.50	5.33	10.75	12.35	
33		164-6.5	54.03	4.16	10.50	12.02	X=Cl
			53.89	4.27	10.27	11.96	13.29 13.48
34		159.5-61	46.31	3.56	9.00	10.30	X=Br
			46.08	3.29	8.78	10.29	23.68 23.59
35		168.5-70	51.97	4.00	13.16	11.56	
			52.11	4.04	13.00	11.43	

36		144.5-6	47.85 3.35 9.30 10.65 X=Cl 23.54 47.95 3.48 9.29 10.88 23.66
37		187-8	61.20 4.60 7.51 8.60 X=Cl 9.51 61.22 4.60 7.48 8.59 9.28
38		151.5-3	64.58 6.19 10.76 12.32 64.48 6.08 11.02 12.18
39		147-8.5	64.58 6.19 10.76 12.32 64.66 6.23 10.61 12.33
40		140	59.07 4.96 10.60 12.13 59.25 5.03 10.48 12.22
41		168.5-70	48.01 4.03 8.61 9.86 X=Br 24.57 48.18 4.19 8.75 10.02 24.68

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42		172.5-4	53.49 4.17 8.91 10.20 53.41 4.08 8.99 10.12
43		101.5-2	67.51 7.33 9.26 10.60 67.50 7.28 9.18 10.66
44		138-40	60.84 5.84 10.14 11.60 61.06 6.12 10.01 11.76
45		161.5-2.5	62.04 6.25 9.65 11.04 62.28 6.33 9.81 11.03
46		136-7	59.07 4.96 10.60 12.13 58.95 4.88 10.49 12.30
47		180-2	48.01 4.03 8.61 9.86 X=Br 24.57 47.86 4.01 8.43 9.81 24.69

48		210-2	41.94 3.52 7.53 8.61 X=I 34.10 41.64 3.28 7.41 8.56 34.36
49		188-91	53.59 4.50 14.43 11.01 53.81 4.72 14.69 10.84
50		219-22	49.53 3.84 8.89 10.17 X=Cl 22.50 49.19 3.76 8.78 10.06 22.76
51		159-61	65.66 6.61 10.21 11.69 65.47 6.55 10.30 11.83
52		193-8	57.04 5.13 9.50 10.88 X=Cl 12.03 57.15 5.28 9.75 10.68 12.15
53		215-6	49.56 4.46 8.26 9.45 X=Br 23.56 49.69 4.60 8.08 9.58 23.38

54		190-1	62.09 4.95 7.24 8.29 X=Cl 9.17 61.98 4.99 7.26 8.31 9.08
55		176-8	68.89 5.44 9.45 10.82 68.91 5.58 9.27 10.88
56		174-6	47.85 3.35 9.30 10.65 X=Cl 23.54 47.71 3.29 9.27 10.72 23.61
57		184-6	49.53 3.84 8.89 10.17 X=Cl 22.50 49.54 3.76 8.72 10.11 22.59

The compounds obtained according to the present invention /885 have outstanding herbicidal and germicidal effects, as seen from the test examples presented below, and their application as agricultural chemicals are promising. To use the compounds of the present invention as agricultural chemicals, the use of carriers presented in, for example, Japanese Patent Application No. 50-16211 is recommended.

Test Example 1            A water-immersed-soil treatment test

In 1/5000-are [100 m<sup>2</sup>] Wagner pots were placed paddy soil, on top of which soil with the seeds of *Panicum crusgalli* and *Rotana indica* mixed in it was placed. Paddy-rice plants (in the 3-leaf stage) were transplanted into the pots, after which the water depth in the pots was maintained at 3 cm. Five days later, granules of the compounds having the compound numbers shown in Table 2 below were scattered evenly over the water surface at rates of 10 g and 30 g per are in terms of the active ingredient content in each compound. During the three days following the treatment, the water level was reduced by 3 cm per day, after which no water-leaking treatment was carried out. Twenty-five days after the chemical treatment, the chemicals' herbicidal effects and effects on the paddy-rice plants were examined. The results are shown in Table 2. The evaluation criteria are as shown below.

Criteria for herbicidal effect

0	nil
1	slight
2	small
3	moderate
4	severe
5	extremely severe (withered)

Criteria for effect on crops

0	no damage
1	slight damage
2	small damage
3	moderate damage
4	severe damage
5	withered



TABLE 2

Compound No.	Chemical content g/a	Herbicidal Effect		Effect on Rice Plants
		Panicum crusgalli	Rotana indica	
1	30	4	5	0
	10	3	5	0
3	30	4	5	0
	10	3	4	0
5	30	5	5	0
	10	4	5	0
6	30	5	5	0
	10	5	5	0
9	30	4	5	0
	10	3	4	0
12	30	4	4	0
	10	2	4	0
13	30	4	5	0
	10	3	4	0
15	30	5	5	0
	10	4	5	0
16	30	5	5	0
	10	5	5	0
17	30	5	5	0
	10	4	5	0
18	30	5	5	0
	10	5	5	0
19	30	5	5	0
	10	5	5	0
23	30	5	5	0
	10	5	5	0
27	30	5	5	0
	10	5	5	0
30	30	4	5	0
	10	3	5	0
31	30	5	5	0
	10	4	5	0
33	30	5	5	0
	10	5	5	0
36	30	5	5	0
	10	5	5	0
37	30	5	5	0
	10	5	5	0
38	30	4	5	0
	10	3	4	0
40	30	5	5	0
	10	5	5	0
43	30	5	5	0
	10	4	5	0
45	30	5	5	0
	10	5	5	0
46	30	5	5	0
	10	5	5	0
48	30	5	5	0
	10	5	5	0
51	30	5	5	0
	10	4	5	0
52	30	5	5	0
	10	5	5	0
54	30	5	5	0
	10	5	5	0
55	30	4	5	0
	10	3	5	0
Untreated zone	-	0	0	0

Test Example 2: A field soil treatment

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After 1/5000-are Wagner pots were filled with field soil, wheat, soybeans, and corn were sowed 2 to 3 cm from the soil surface, which was followed by the sowing of the seeds of *Digitaria adscendens* and *Galinsoga parviflora* in the surface layer of the soil. Thereafter, the compounds having the compound numbers shown in Table 3 below in a water-dispersible-powder form were diluted in water and sprayed uniformly over the soil surface at rates of 10 g and 30 g per are in terms of the active ingredient content in each compound. Twenty-five days after the chemical treatment, the chemicals' herbicidal effects on *Digitaria adscendens* and *Galinsoga parviflora* were examined. At the same time, damage to wheat, soybeans, and corn from the chemicals was examined. The evaluation was conducted using the same criteria as in Test Example 1. The results are shown in Table 3.

TABLE 3

Compound No.	Chemical content G/a	Herbicidal Effect		Effect on Crops		
		Digitaria adscendens	Galinsoga parviflora	Wheat	Soybeans	Corn
2	30	4	5	0	0	0
	10	3	4			
3	30	5	5	0	0	0
	10	4	5			
4	30	5	5	0	0	0
	10	4	5			
7	30	5	5	0	0	0
	10	5	5			
8	30	5	5	0	0	0
	10	5	5			
10	30	4	5	0	0	0
	10	3	4			
12	30	4	4	0	0	0
	10	2	3			
16	30	5	5	0	0	0
	10	5	5			
22	30	5	5	0	0	0
	10	4	5			
25	30	5	5	0	0	0
	10	5	5			
26	30	5	5	0	0	0
	10	5	5			
32	30	5	5	0	0	0
	10	5	5			
34	30	5	5	0	0	0
	10	5	5			
39	30	5	5	0	0	0
	10	3	5			
41	30	4	5	0	0	0
	10	3	5			
44	30	5	5	0	0	0
	10	5	5			
46	30	5	5	0	0	0
	10	5	5			
47	30	5	5	0	0	0
	10	5	5			
50	30	5	5	0	0	0
	10	4	5			
52	30	5	5	0	0	0
	10	5	5			
53	30	5	5	0	0	0
	10	4	5			
Untreated zone	-	0	0	0	0	0

### Test Example 3: A foliage treatment

Field soil was packed in 1/5000-are Wagner pots, and millet, *Digitaria adscendens*, and Japanese radish were sowed and grown in them. Emulsions of the compounds having the compound numbers shown in Table 4 were diluted with water so as to prepare diluted solutions having active-ingredient concentrations of 0.1 % and 0.3 %. Each diluted solution was sprayed on foliage with a small pressurized sprayer at a spraying rate of 10 L per are.

Twenty days after the treatment, the herbicidal effects were studied according to the criteria used in Test Example 1. The results are shown in Table 4. When the chemicals were sprayed, the millet and *Digitaria adscendens* were in the 2 to 3 leaf stage, and the Japanese radish was in the first-leaf stage. Here, the Japanese radish was used as a substitute for broad-leaf weeds.

TABLE 4

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Compound No.	Chemical content (%)	Herbicidal Effect		
		Millet	Digitaria adscendens	Japanese Radish
6	0.3	5	5	5
	0.1	4	5	5
8	0.3	5	5	5
	0.1	4	5	3
11	0.3	5	5	5
	0.1	4	5	4
12	0.3	4	5	4
	0.1	4	5	4
14	0.3	5	5	5
	0.1	4	5	4
20	0.3	5	5	5
	0.1	5	5	5
21	0.3	5	5	5
	0.1	5	5	5
23	0.3	5	5	5
	0.1	4	5	4
25	0.3	5	5	5
	0.1	5	5	5
33	0.3	5	5	5
	0.1	5	5	5
35	0.3	5	5	5
	0.1	4	5	5
41	0.3	4	4	4
	0.1	2	3	3
46	0.3	5	5	5
	0.1	4	5	4
49	0.3	5	5	5
	0.1	4	5	5
52	0.3	5	5	5
	0.1	4	4	3
53	0.3	4	5	5
	0.1	3	4	3
56	0.3	5	5	5
	0.1	4	5	5
Untreated zone	-	0	0	0

## Test Example 4

Twenty-five milliliters each of suspensions (500 ppm) of the compounds having the compound numbers shown in Table 5 below were sprayed over green beans, which were planted in 9 cm-diameter pots and in the true-leaf-developing stage, on a turntable.

After they were air-dried, 6 mm-diameter agar discs in which *Botrytis cinerea* had been cultivated were placed on the true leaves to inoculate them. The plants were left standing for 4 days in a 23°C humidified chamber so as to bring about the outbreak of the disease, and the degree of the outbreak was examined. According to the following equation, the control rates were calculated and are shown in Table 5.

Control rate (%) = [(A) - degree of disease outbreak in the chemical-treated zone] ÷ degree of disease outbreak (A) in the untreated zone x 100

TABLE 5

Compound No.	Concentration (ppm)	Control Rate (%)
28	500	100
29	"	100
56	"	84.0
57	"	78.0
Untreated zone	-	0

#### Test Example 5

Paddy rice plants (Kind: Kinnanpu) that had grown to the 5 to 6 leaf stage in 9-cm pots in a hot house were cut so as to set their height to 20 to 30 cm, and suspensions (500 ppm) of the compounds below were sprayed over the plants on a turntable at a rate of 20 mL/pot. After they were air-dried, they were inoculated with the fungus body of *Pellicularia sasakii*, which had been cultured in a wheat bran medium for seven days, at the roots of the rice plants. Each pot was covered entirely with a plastic bag with holes so as to maintain the humidity at a constant level

and then left standing in a constant-temperature chamber set to 25 to 27°C. Twenty days later, the degree of the outbreak of the disease was examined, and, according to the following equation, the prevention rates were calculated. The results are shown in Table 6.

Prevention rate (%) = [(A) - degree of disease outbreak in the treated zone] ÷ degree of disease outbreak (A) in the untreated zone x 100

TABLE 6

Compound No.	Concentration (ppm)	Prevention Rate (%)
29	500	98.1
57	"	73.2
Untreated zone	-	0

#### Test Example 6

Paddy rice plants (Kind: Kinnanpu) planted in 9-cm pots and grown to the 4 to 5 leaf stage in a hot house were sprayed with 500 ppm-emulsions of the following compounds on a turntable at a rate of 20 mL per pot. After air-drying, a suspension of separately cultured *Chochliobolus miyabeanus* spores was sprayed to inoculate the plants, and the pots were left standing in a 25 to 27° C constant-temperature chamber in a humidified condition. Forty-eight hours later, the number of the spots caused by the disease was examined, and the prevention rates were calculated according to the following equation. The results are shown in Table 7.

Prevention rate (%) = [(A) - number of spots caused by the disease

in a treated zone]÷number of spots caused by the disease in an untreated zone x 100

TABLE 7

Compound No.	Concentration (ppm)	Prevention Value
28	500	91.8
29	"	85.9
Untreated zone	-	0